Computation Modeling of Localized Corrosion Stability on Wetted SS316L at 25 and 95°C

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For corrosion resistant materials exposed to lowtemperature atmospheric environments, the corrosion mode of highest risk is expected to be localized corrosion (pitting, crevice, stress-corrosion cracking) due to accumulation of aggressive species within thin solution layers and/or formation of occluded local geometries. The stability of such a localized corrosion site requires that the corroding site (anode) must dissolve at a sufficient high rate to maintain the critical chemistry, and a robust cathodic area (cathode) must exist that can provide sufficient cathodic current.^[1] The characteristics of both the anode and the cathode depend on a large number of physiochemical variables (e.g., temperature, water layer thickness, concentration. etc) electrochemical parameters (i.e., cathodic and anodic polarization behavior). The effects of all these parameters add significantly to the dimensionality of the problem and a systematic study of these parameters is thus more tractable computationally than experimentally.

The objective of this study was to computationally characterize the stability of such a local corrosion site and explore the effects of physiochemical and electrochemical parameters on that stability. The overall goal is to contribute to the establishment of a scientific basis for the prediction of the stabilization of localized attack on wetted, corrosion resistant material surface.

A localized corrosion site, illustrated in Figure 1, consists two parts: a) the external wetted surface (cathode) and b) the crevice (anode). This study computationally separated the two and modeled them individually, linking them through the imposition of a common fixed potential at the junction point (i.e., the mouth of the crevice). An objected-oriented computational code, CREVICER, developed at UVa, was extended to study separately both the wet surface (cathode) and the crevice (anode). [2,3] SS316L was chosen as the material of interest.

The Cathode: The ability of the external wet surface to serve as a cathode was investigated using a full factorial design of water layer thickness (WL), chloride concentration [Cl] and length of cathode (Lc). The effect of electrochemical parameters including the exchange current density $(i_{o,c})$ and Tafel slope (β_c) of oxygen reduction, the anodic passive current density (i_p) (on the cathodic surface), and repassivation potential $\boldsymbol{E}_{\boldsymbol{rp}}$ were studied as well using a three-level full factorial designs of [Cl] and Lc with a fixed WL of 25µm. Significant effects on the total net cathodic current (I_{net}) were found upon varying either WL, Lc, [Cl⁻], $i_{o,c}$, β_c , or E_{rp} , whereas i_p in the studied range was found to have little impact. Inet increased by a factor of 5 times or more when the temperature was increased from 25 to 95°C. As shown in Figure 2, Inet asymptotically approached maximum values (I_{max}) when Lc increased to critical minimum values. I_{max} can be used to determine the stability of coupled localized corrosion and the critical Lc provides important information for experimental design and corrosion protection.

The Anode: In this portion of the paper calculations were conducted to determine the total anodic current (I_{LC}) that is required by a localized corrosion site as a function of relevant chemical, electrochemical, and metallurgical parameters. The initial set of calculations of I_{LC} assumed constant crevice chemistry. For these conditions studied, only crevices tighter than 10 μ m would be stable. Figures 3 compares I_{LC} with the range of current obtained from the external cathode. Computations that allow chemistry changes are being conducted. In these computations, the electrochemical kinetics changed as a function of local crevice solution pH. The hydrolysis was determined by $[Cr^{3+}]$.

References:

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- 2. K.C. Stewart, Ph.D. Dissertation, University of Virginia, 1999
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Figure 1. Diagram showing the two components modeled

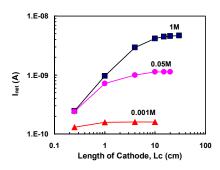


Figure 2. Total net cathodic current I_{net} got saturated as length of cathode increased to a critical value. The speed of saturation depends highly on [Cl⁻] (shown) as well as WL.

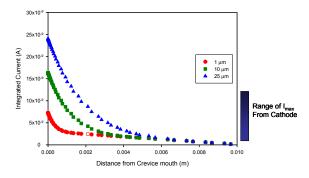


Figure 3. Integrated current along the crevice, I_{LC} intersect the y-axis.